THE EFFECTS OF EXCHANGEABLE BASES ON THE FIRED PROPERTIES OF FIRE CLAYS

BY

JAMES ADAMSON CROOKSTON

B. S., Missouri School of Mines and Metallurgy, Rolla, Missouri, 1942

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CERAMIC ENGINEERING
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INTRODUCTION

The behavior of refractory fire clays at high temperatures and under service conditions is influenced by the presence of minor constituents. It is the purpose of this study to determine the effects of one class of minor constituents, exchangeable bases or alkalies, on several Missouri fire clays.

The problem appeared to resolve itself into three natural parts: 1—determination of some characteristics of the clays under investigation; 2—determination of the effects of exchangeable bases on the fired mineralogical composition of the clays; 3—determination of the effects of the exchangeable bases on some physical properties.

EXPERIMENTAL PROCEDURE

The mineralogical compositions of various size fractions of the clays were determined by x-ray and petrographic examination. Base exchange capacities of coarse and fine ground samples of the clays were obtained by leaching the clays with ammonium acetate, followed by washing with absolute methyl alcohol. The replaceable ammonia was determined by the Kjeldahl method. The exchangeable bases present in the raw clays were quantatively determined with the flame photometer. The free quartz in the clays and in some size fractions was determined by quantitative x-ray analysis. Slaking characteristics were determined by dry- and wet-sieve analysis.

The clays were saturated with various exchangeable bases by first preparing them in the H-form by acid leaching, followed by leaching with weak solutions of the desired alkalies. The alkalies present in the treated clays were quantitatively determined with the flame photometer. Samples of each raw clay and its various forms were fired together in a Glo-Bar furnace to 1,300 degrees C. and 1,400 degrees C for approximately 16 hours. Quantative and

quantitative x-ray analyses were made on the fired samples, and the results were checked petrographically in some cases. Differential thermal analysis curves were made for the raw and treated clays.

To provide a basis for discussion of the results, phase equilibrium studies were made of the clays and their forms, with the following assumptions: 1—Titania was taken as Alumina; 2—Ferric Oxide was taken as Silica; 3—Soda and Potash were taken as a total of Soda; 4—Calcia and Magnesia were ignored. These assumptions, made on the basis of their phase diagrams, make it possible to express the clay compositions in three components: Silica, Alumina, and Soda.

Large batches of the forms of Fulton Plastic fire clay were prepared in the manner previously described, and test specimens were dry-pressed. The progress of linear shrinkage of H- and K-forms was determined over the range 70 to 2,000 degrees F. The thermal expansion of bars fired at 1,300 degrees C and 1,400 degrees C was measured. The modulus of elasticity of bars fired to these temperatures was determined by a sonic method. These were then cut to approximately 3-inch lengths and their deformation was measured at 1,425 degrees C under a load of 25 p. s. i.

DISCUSSION OF RESULTS

All of the clays contained kaolinite as the principal mineral, with varying amounts of free quartz. Burley clay also contained some diasporite. Slaking characteristics varied, with Missouri Flint clay the least readily slaked, Semi-Flint next, and Fulton Plastic, Semi-Plastic, and Burley clays readily slaked. The base-exchange capacities for Missouri Flint and Burley clays were nearly equal at 6-7 m.e., with those of the other clays similar at approximately 12 m.e. The difference in these values for the coarse and fine ground forms was small, with the fine ground clays apparently slightly greater. Quartz appeared to occur in larger amounts in the coarser fractions of all clays, although it was fairly well distributed in all fractions in the Fulton Plastic and Semi-Plastic clays. X-ray patterns and differential thermal analysis curves in-

dicated a basic difference in the clay mineral material present in the various clays, with that of the Flint and Semi-Flint clays being closest to kaolinite and the others less well organized.

The character of the differential thermal analysis curves of the clay forms appeared to be unchanged by the presence of the exchangeable bases. The principal minerals in the fired clays were mullite and cristobalite. The mullite content appeared to be little affected by the exchangeable bases present, while the cristobalite content was strongly affected. The K-ion reduced the cristobalite content a good deal and Na-ion was quite effective. There was less Na-ion present by weight due to the difference in atomic weight. The Ca- and Mg-ions did not appear to have much effect. There was little difference between the raw and H-forms. The K-ion appeared to have a strong color bleaching effect with the Na-ion having a lesser effect in this respect. These effects were greatest for the clays with higher base-exchange capacities.

The firing shrinkage characteristics were not affected by the presence of the exchangeable bases. The thermal expansions of the clay forms fired to 1,400 degrees C were quite different, with the H- and raw-forms showing a break in their curves at 400 degrees F due to the presence of cristobalite. The Na-form showed a very slight break and the K-form showed no break. The thermal expansions of those fired to 1,300 degrees C were quite similar to each other and did not show any definite break in their curves. The modulus of elasticity varied, with the alkali forms being higher at both temperatures than the H- and raw-forms, due to more glass formation. The difference was greater at 1,300 degrees C than at 1,400 degrees C, as predicted by the phase study. The deformation under load was only slightly higher for the alkali forms than for the H- and raw-forms.

VITA

James Adamson Crookston was born in Benld, Illinois, on December 8, 1919. He attended the elementary and high schools in this city and graduated in 1938. He entered the Missouri School of Mines and Metallurgy at Rolla, Missouri, in the fall of the same year, and received a B. S. degree in Ceramic Engineering in 1942. He worked for two years with the AC Spark Plug Division, General Motors Corporation, and then enlisted in the US Navy. He was separated from the service in 1946, and in the fall of that year entered the Missouri School of Mines and Metallurgy at Rolla, Missouri. He received an M. S. degree in Ceramic Engineering in 1947. He matriculated at the University of Illinois in September, 1947, as the recipient of the A. P. Green Fire Brick Company Fellowship in Refractories.

He is a member of the American Ceramic Society and the Institute of Ceramic Engineers. He is also a member of Tau Beta Pi, Sigma Xi, and Keramos honorary societies.

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